PREPARATIONS OF DIALKYLAZOXYBENZENES AND THEIR DERIVATIVES[1]

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ABSTRACT

The three isomeric symmetrical dimethylazoxybenzenes have been prepared in very good yield by oxidation of the corresponding azobenzenes with peracetic acid. 2,2′- and 4,4′-Diethylazoxybenzenes have been synthesized by oxidation of the azobenzenes and reduction of the ethylnitrobenzenes. The diethylazoxybenzenes were also reduced to the corresponding azo- and hydrazo-benzene derivatives.

INTRODUCTION

Some work on the oxidation of mono- and di-methylazobenzenes has been reported in the chemical literature. For instance, 2- and 4-methylazobenzene have been oxidized by means of peracetic acid (1, 2) and the rates of oxidation of some dimethylazobenzenes with perbenzoic acid have been determined (3). One object of this work was to prepare dimethylazoxybenzenes from the azobenzenes by oxidation with hydrogen peroxide in glacial acetic acid.

Schultz reported in an earlier paper (4) that 2- and 4-nitroethylbenzenes are reduced to the corresponding diethylazobenzenes by zinc dust and sodium hydroxide, and recently Wheeler (5) has studied the polarographic reduction of these nitroethylbenzenes. In the present work, new diethylazoxybenzenes were prepared both from the nitroethylbenzenes by reduction with reducing sugars in alkaline medium, and from the diethylazobenzenes by oxidation with peracetic acid.

DISCUSSION

2,2′-, 3,3′-, and 4,4′-Dimethylazoxybenzenes were prepared in very good yield from the corresponding azobenzenes by oxidation with peracetic acid. Some results are shown in Table I. The 2,2′-dimethylazobenzene proved difficult to oxidize, a great excess of hydro-

TABLE I
Peracetic acid oxidations of dialkylazobenzenes*

Azobenzene, g		H_2O_2, ml	Time, hr	Temp., ° C	Azoxybenzene yield, %
2,2′-Dimethyl-	0.510	25	$17\frac{1}{2}$	65–75	70
2,2′-Dimethyl-	1.337	25	21	65–77	68
2,2′-Dimethyl-	0.423	30	2	61–66	91
3,3′-Dimethyl-	0.407	25	3	61–65	87
4,4′-Dimethyl-	0.405	15	1	65–70	89
4,4′-Dimethyl-	0.398	15	5	65–66	70
2,2′-Diethyl-	0.307	5	20	65–70	66
2,2′-Diethyl-	0.789	5	$24\frac{1}{2}$	80–90	71
2,2′-Diethyl-	1.858	10	$\frac{1}{2}$	Reflux	64
2,2′-Diethyl-	0.408	25	4	55–65	40
2,2′-Diethyl-	0.517	10	$6\frac{1}{2}$	60–70	84
4,4′-Diethyl-	0.200	5	$1\frac{1}{2}$	65–70	52
4,4′-Diethyl-	0.200	5	5 minutes	Reflux	67

*Glacial acetic acid (50 ml) was used in all oxidations.

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gen peroxide being necessary to obtain the azoxybenzene in over 90% yield. The azo linkage in this case is sterically hindered by the methyl groups and this impedes oxidation. A similar effect was encountered previously with the oxidation of 2,2′-dichloroazobenzene (6, 7). Prolonged oxidation of the dimethylazobenzenes led in each case to decomposition and lower yields of the dimethylazoxybenzenes.

2,2′- and 4,4′-Diethylazoxybenzenes were also prepared from the corresponding azobenzenes by oxidation with hydrogen peroxide in glacial acetic acids and fair yields were achieved. The details are found in Table I. To prepare 2,2′-diethylazoxybenzene in over 60% yield, either an extended period of reaction or elevated temperature was necessary, and this can be attributed to steric hindrance by the bulky ethyl groups.

The diethylazoxybenzenes were synthesized also by reduction of the nitroethylbenzenes with reducing sugars. The sterically hindered 2-nitroethylbenzene was very difficult to reduce as expected. With dextrose, over 80% of the starting material was recovered, whereas when lactose was used more reduction occurred. In both cases, 2,2′-diethylazoxybenzene and 2-ethylaniline were obtained in very low yield. Attempts were also made to reduce 2-nitroethylbenzene with sodium arsenite in alkaline medium but these were not successful. Reductions of 4-nitroethylbenzene with dextrose or lactose gave low yields of 4,4′-diethylazoxybenzene. Some results are given in Table II.

TABLE II

Reductions of nitroethylbenzenes

Nitrobenzene, moles		Reducing agent, moles		NaOH, moles	H_2O, ml	Time, hr	Temp., ° C	Products, %		
								Rec. Nitro	Azoxy	Amine
2-Ethyl-	0.17	Dextrose	0.13	0.75	285	1½	60–70	80.4	4.6	Nil
2-Ethyl-	0.17	Dextrose	0.13	1.00	285	2	65	80.4	2.4	5.5
2-Ethyl-	0.17	Lactose	0.13	0.75	285	2	60–70	65.2	1.7	4.1
2-Ethyl-	0.17	Lactose	0.13	0.75	285	1	80–85	56.5	1.5	5.2
2-Ethyl-	0.17	Lactose	0.13	0.75	280	2	55–60	61.0	8.3	5.0
2-Ethyl-	0.17	As_2O_3	0.15	0.75	150*	3	82	95.6	Nil	Nil
4-Ethyl-	0.033	Dextrose	0.025	0.14	57†	1	75	18.2	5.6	Nil
4-Ethyl-	0.033	Lactose	0.025	0.14	57†	1	78	16.0	4.8	Nil

*Methanol (65 ml).
†Methanol (25 ml).

The diethylazoxybenzenes described in this work were synthesized for the first time. The structure of 2,2′-diethylazoxybenzene was established by reduction to 2,2′-diethylhydrazobenzene and oxidation of the latter to the known 2,2′-diethylazobenzene. Confirmation of the structure was also achieved by reduction to 2-ethylaniline with stannous chloride. The structure of 4,4′-diethylazoxybenzene was determined by conversion to the known 4,4′-diethylazobenzene via the new hydrazobenzene.

The compounds 2,2′-diethylazo- and azoxy-benzene are of interest since the bulky ethyl groups should present steric hindrance to coplanarity and this effect can be detected by ultraviolet absorption spectroscopy. Badger and Buttery (8) showed by a model that 2,2′-dimethylazoxybenzene must be non-coplanar and observed a hypsochromic shift of about 20 mμ in the *K*-band (conjugation) of the ultraviolet spectrum on conversion of 2,2′-dimethylazobenzene to the azoxybenzene. Here conjugation is inhibited and the *K*-band should occur at shorter wavelength. Gore and Wheeler (9) have reported that the hypsochromic shift in the above case is 18 mμ. The ultraviolet spectra of 2,2′-diethylazo- and azoxy-benzene are compared in Fig. 1. The introduction of the oxygen atom into

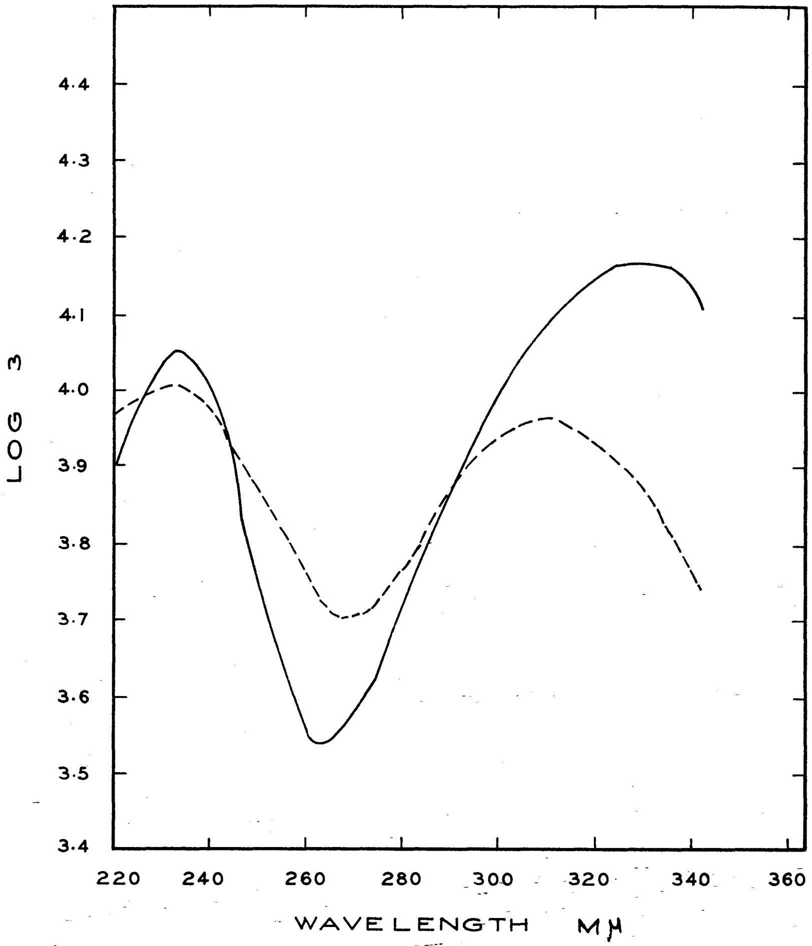

FIG. 1. Absorption spectra of 2,2′-diethylazobenzene (—) and 2,2′-diethylazoxybenzene (– – –).

2,2′-diethylazobenzene caused a hypsochromic shift of 21 mμ in the *K*-band due to inhibited conjugation. Spectral data for the diethylazoxybenzenes and their derivatives are given in Table III.

The ultraviolet spectrum of azobenzene has been shown to possess a *K*-band at 320 mμ (ε 17,300) (10). In Table IV, the shifts and changes in intensity of the *K*-bands for dimethyl- and diethyl-azobenzenes are compared. The *K*-bands of the 2,2′-dialkylazobenzenes undergo bathochromic shifts accompanied by decreases in intensity. The results indicate that the more bulky ethyl group leads to increased steric hindrance to coplanarity. If it is assumed that the molecular extinction coefficient of the *K*-band of the 2,2′-disubstituted azobenzenes will be as high as that of the 4,4′-disubstituted derivatives in the absence of steric effects, then the degree of non-coplanarity or total deformation angle can be calculated using the method of Braude and Sondheimer (11). The deformation angle for 2,2′-diethylazobenzene is 33° compared to 23° for 2,2′-dimethylazobenzene as reported by Gore and Wheeler (10). The deformation angle should increase with the effective size of the substituent and such is the case here.

TABLE III

Absorption spectra of diethylazoxy-, azo-, and hydrazo-benzenes*

	Bands					
Substituent	*E*		*K*		*R*	
Azoxybenzenes						
2,2′-Diethyl-	234	(10,600)	309	(9,300)	None	
4,4′-Diethyl-	236	(13,500)	334	(20,700)	None	
Azobenzenes						
2,2′-Diethyl-	235	(11,300)	330	(14,800)	460	(560)
4,4′-Diethyl-	236	(13,900)	331	(21,000)	440	(1,000)
Hydrazobenzenes						
2,2′-Diethyl-†	245	(18,500)	287	(3,200)	None	
2,2′-Diethyl-‡	245	(17,700)	289	(5,200)	450	(210)
4,4′-Diethyl-§	248	(21,700)	298	(4,500)	437	(85)
4,4′-Diethyl-‖	244	(9,700)	330	(6,700)	—	—
4,4′-Diethyl-¶	236	(14,800)	330	(19,800)	442	(960)

*Wavelength is recorded in mμ, and the molecular extinction coefficients, ε, values are shown in parentheses.

†Freshly prepared sample kept in vacuum desiccator.

‡Sample kept in air for several weeks. A *K*-band was also present, λ_{max}, 330 mμ (ε, 3200).

§Freshly prepared sample kept under nitrogen.

‖Sample kept for several days in air.

¶Sample kept for 2 weeks in air.

TABLE IV*

Shifts and intensity changes of the *K*-bands of dialkylazo- and azoxy-benzenes

	Azobenzenes		Azoxybenzenes	
Substituents	Shift, mμ	Intensity change	Shift, mμ	Intensity change
2,2′-Dimethyl-	+10	−900	−11	−3400
2,2′-Diethyl-	+10	−2500	−14	−5200
4,4′-Dimethyl-	+10	+2000	+ 7	+3600
4,4′-Diethyl-	+11	+3700	+11	+6200

*The results for the dimethylazo- and azoxy-benzenes are those of Gore and Wheeler (9, 10).

The *K*-band in the ultraviolet spectrum of azoxybenzene has been shown to occur at 323 mμ (ε 14,500) (9). The data in Table IV shows that the *K*-bands of 2,2′-dimethyl- and diethyl-azoxybenzene exhibit hypsochromic shifts together with decreases in intensity. There is, however, more pronounced steric hindrance to coplanarity in the 2,2′-diethylazoxybenzene. The deformation angle for the latter compound is 48° compared to 38° for the 2,2′-dimethylazoxybenzene (9). There is greater hindrance in the 2,2′-dialkylazoxybenzenes than the azobenzenes due to the presence of the oxygen atom of the azoxy group. Moreover, our results show that for both the azoxy- and the azo-benzenes the replacement of the methyl groups by ethyl groups causes an increased distortion of 10° in the molecule. The total deformation angle is also increased by 15° for both 2,2′-dimethyl- and 2,2′-diethyl-azobenzene on passing to the corresponding azoxybenzene, due to the insertion of the coordinated oxygen atom.

Data concerning the *K*-bands of the ultraviolet spectra of the 4,4′-dialkylazo- and azoxy-benzenes is also given in Table IV. The *K*-band of both 4,4′-dimethyl- and diethylazobenzene showed a bathochromic shift and increased intensity. If the ethyl groups contribute equally to the polarization of the molecule, the results indicate that each ethyl group causes a bathochromic shift of 5.5 mμ, and an increase in intensity of 1850 compared to 5 mμ, and 1000 per methyl group. Similar results were obtained with 4,4′-dimethyl- and diethyl-azoxybenzenes, the increases in intensity of the *K*-bands being greater. These results show that for the 4,4′-dialkylazo- and azoxy-benzenes, the electron-releasing inductive effect of the alkyl groups is the important factor rather than the hyperconjugative effect.

The ultraviolet spectra of the diethylhydrazobenzenes possess two bands, a high intensity *E*-band at 245–250 mμ, and a low intensity band at about 285–300 mμ (Table III). Oxidation of the diethylhydrazobenzenes to the azobenzenes causes the latter band to disappear and a high intensity *K*-band to occur in the ultraviolet spectrum. The formation of the azo group is also shown by the appearance of a low intensity *R*-band in visible spectrum.

The diethylhydrazobenzenes showed quite different sensitivities to air oxidation. After it had been standing in air for several weeks the 2,2′-diethylhydrazobenzene turned pink but was only slightly oxidized. Furthermore, it was not completely oxidized to the azobenzene when boiled in alcoholic solution for 10 minutes. In contrast, 4,4′-diethylhydrazobenzene was extremely sensitive to oxidation, turning deep yellow when in contact with air for a few minutes and oxidizing to the azobenzene completely after 2 weeks.

The resistance of 2,2′-diethylhydrazobenzene to air oxidation can be accounted for by steric hindrance, whereas in 4,4′-diethylhydrazobenzene this effect is not operative. Recent results (12) have shown that the sterically hindered 2,2′-diethoxyhydrazobenzene can only be converted to the azobenzene by refluxing with peracetic acid.

EXPERIMENTAL*

Materials

The nitroethylbenzenes used in this work for reductions were commercially available samples.

Reductions of Nitroethylbenzenes

Since essentially the same procedures were used in all reductions carried out using the sugars and sodium arsenite, only one procedure for each method is described.

Reduction of 4-Nitroethylbenzene with Dextrose

4-Nitroethylbenzene 5.0 g (0.033 mole) was dissolved in methanol (25 ml), and sodium hydroxide 5.8 g (0.14 mole) in water (57 ml) was added. Dextrose 4.56 g (0.025 mole) was then added in portions and the mixture stirred vigorously and heated at 75° for 1 hour. The reaction mixture was steam distilled to give a distillate containing a yellow liquid. The distillate was acidified with hydrochloric acid and the yellow liquid separated off, dried, and purified by distillation to give recovered 4-nitroethylbenzene, b.p. 240° at 758 mm (lit. b.p. 245–246° at 760 mm) (13), yield, 18.2%. The acid layer was made alkaline with sodium hydroxide and allowed to stand overnight in the refrigerator, but no 4-ethylaniline separated out. The mixture in the flask after steam distillation contained an oily liquid which was extracted with ether to give a yellow extract. The latter was dried and removal of solvent left a reddish liquid, which was distilled under reduced pressure to give a deep yellow oil, b.p. 244° at 16 mm. When it had been cooled in the refrigerator, the oil solidified to give orange-yellow crystals, m.p. 16–17°. Anal. Calc. for $C_{16}H_{18}N_2O$: C, 75.56%; H, 7.13%; N, 11.01%. Found: C, 76.30%; H, 7.14%; N, 11.28%. The product was 4,4′-diethylazoxybenzene, yield, 5.6%. Infrared spectrum bands at: 3.08, 3.42, 3.50, 3.51, 3.61, 5.98, 6.28, 6.74, 6.90, 7.10, 7.60, 7.69, 7.88, 8.61, 8.98, 9.45, 9.51, 9.85, 10.32, 10.92, 11.82, and 14.78 μ.

In the reduction of 2-nitroethylbenzene, besides the azoxybenzene, some 2-ethylaniline was formed and identified by conversion to the acetyl derivative.

Reduction of 2-Nitroethylbenzene with Sodium Arsenite

2-Nitroethylbenzene 25.9 g (0.17 mole) was dissolved in methanol (65 ml), and sodium hydroxide 30.0 g (0.75 mole) in water (125 ml) was added. Then arsenic trioxide 29.7 g (0.15 mole) as a paste mixed with water (25 ml) was added in portions to the mixture, which had been heated to 60°. The reaction mixture was vigorously stirred throughout and the reaction carried out at 82° for 3 hours. Steam distillation gave recovered 2-nitroethylbenzene, in the acidified distillate, b.p. 223–225° at 756 mm (lit. b.p. 227–228° at 760 mm) (13), yield, 95.6%. No other products were isolated.

**All melting points are uncorrected.*

Preparations of Dialkylazobenzenes

The dimethylazobenzenes were prepared from the appropriate nitrotoluenes by reductions with zinc dust and sodium hydroxide. Reductions of 2- and 4-nitroethylbenzene by the method described by Schultz (4) gave 2,2′-diethylazobenzene, red needles, m.p. 45–46°. Anal. Calc. for $C_{16}H_{18}N_2$: N, 11.75%. Found: N, 11.66%. (Lit. m.p. 46.5° (4), and 4,4′-diethylazobenzene, orange needles, m.p. 59–60°.) Found: N, 11.47%. (Lit. m.p. 63° (4).)

Peracetic Acid Oxidations of Dialkylazobenzenes

Only one oxidation will be described since essentially the same procedure was employed in all cases.

Oxidation of 2,2′-Diethylazobenzene

2,2′-Diethylazobenzene (1.858 g) was dissolved in glacial acetic acid (50 ml) and 30% hydrogen peroxide (10 ml) added. The red solution was then refluxed for 30 minutes (at which time the color had turned to yellow) and poured into an excess of cold water. The mixture was cooled and extracted with ether to give a yellow extract, which was dried and the solvent removed. The residue, a deep yellow oil, was purified by distillation under reduced pressure, b.p. 168–169° at 2.7 mm. When cooled in the refrigerator, the oil solidified to give orange-yellow crystals, m.p. 12–13°. The product was 2,2′-diethylazoxybenzene, yield, 64.0%. Anal. Calc. for $C_{16}H_{18}N_2O$: C, 75.56%; H, 7.13%; N, 11.01%. Found: C, 75.62%; H, 7.16%; N, 10.91%. Infrared spectrum bands at: 3.35, 3.50, 3.51, 3.58, 6.34, 6.79, 6.90, 7.30, 7.60, 8.08, 8.43, 8.63, 8.75, 8.92, 9.20, 9.46, 9.69, 10.50, 10.80, 10.90, 11.80, 12.58, 12.91, and 14.91 μ.

In the peracetic acid oxidations of the dimethylazobenzenes, the azoxybenzene separated out as a yellow solid when the reaction solution was cooled after dilution and the product was recrystallized from aqueous ethanol.

Reductions of Diethylazoxybenzenes

2,2′-Diethylazoxybenzene

2,2′-Diethylazoxybenzene (1.313 g) was dissolved in a minimum of ethanol and 40% sodium hydroxide solution (4 ml) added, together with an excess of zinc dust. The mixture was refluxed for 1 hour (at which time all color had disappeared), decanted, and poured into an excess of cold water. A yellow product separated out when the mixture was allowed to stand. This product was washed with water and, to decolorize it, was dissolved in ethanol containing a little glacial acetic acid and warmed in the presence of a little zinc dust. The solution was then poured into cold water to precipitate the colorless product, m.p. 106–108°. Repeated recrystallizations from aqueous ethanol gave 2,2′-diethylhydrazobenzene, colorless needles, m.p. 108–108.5°, yield, 62.8%. Anal. Calc. for $C_{16}H_{20}N_2$: C, 79.95%; H, 8.38%; N, 11.66%. Found: C, 80.08%; H, 8.27%; N, 11.55%. Infrared spectrum bands at: 2.80, 3.30, 3.35, 3.40, 3.48, 6.28, 6.64, 6.71, 6.81, 6.92, 7.33, 7.61, 7.75, 8.05, 8.64, 8.95, 9.52, 9.75, 10.43, 10.68, 11.90, 12.64, 12.97, 13.30, and 14.92 μ. This compound slowly oxidizes in air when it has been left standing and takes on a pinkish color. After preparation it must be dried in a vacuum desiccator and stored there.

2,2′-Diethylazoxybenzene (0.5 g) was treated with an excess of stannous chloride dihydrate and con-concentrated hydrochloric acid for several minutes and the reaction mixture shaken and warmed. The latter was then cooled, diluted with water, and made alkaline. Ether extraction and removal of the solvent gave a dark yellow oil, which was 2-ethylaniline, the infrared spectrum being identical with that of an authentic sample. Acetylation with acetic anhydride also gave 2-ethylacetanilide (from ethanol), m.p. 108–109.5°, alone or with an authentic sample.

4,4′-Diethylazoxybenzene

4,4′-Diethylazoxybenzene (0.352 g) was dissolved in ethanol and 40% sodium hydroxide (1.5 ml) added, together with an excess of zinc dust. The reaction was carried out under a nitrogen atmosphere and the mixture warmed and shaken until all color disappeared. The solution was decanted into an excess of water, the nitrogen atmosphere being maintained throughout. When the solution had been shaken, a colorless product separated out and was collected by very rapid filtration. The substance was 4,4′-diethylhydrazobenzene, which immediately turned pale yellow, m.p. 87–89°, yield, 40.8%. Anal. Calc. for $C_{16}H_{20}N_2$: C, 79.95%; H, 8.38%; N, 11.66%. Found: C, 79.66%; H, 7.64%; N, 11.41%. Infrared spectrum bands at: 2.98, 3.30, 3.35, 3.40, 3.48, 6.20, 6.58, 6.70, 6.88, 7.10, 7.70, 8.02, 8.10, 8.52, 8.70, 9.00, 9.46, 11.78, 12.00, 12.10, 13.87, and 14.45 μ. This reduction, when carried out in air gives a product which turns deep yellow and must be decolorized with glacial acetic acid and zinc dust. 4,4′-Diethylhydrazobenzene oxidizes very rapidly in air and must be stored under a vacuum or nitrogen.

Reductions of Diethylazobenzenes

To 2,2′-diethylazobenzene (0.3 g) in a minimum of ethanol, 40% sodium hydroxide (1 ml) and excess zinc dust were added, and the mixture refluxed for 2 hours. Extraction, using the procedure described for the reduction of 2,2′-diethylazoxybenzene, gave 2,2′-diethylhydrazobenzene, m.p. 107–108°, identity confirmed by infrared spectral analysis.

Reduction of 4,4′-diethylazobenzene with sodium hydroxide and zinc dust using the method employed for the reduction of 4,4′-diethylazoxybenzene gave 4,4′-diethylhydrazobenzene, whose infrared spectrum was identical with that of an authentic sample.

Oxidations of Diethylhydrazobenzenes

2,2′-Diethylhydrazobenzene

2,2′-Diethylhydrazobenzene (0.15 g) was dissolved in ethanol and the solution boiled in air to the point of crystallization. The product was dissolved in ethanol again and the treatment repeated several times to give a mixture of red and colorless crystals. The red product was 2,2′-diethylazobenzene, m.p. 44–46° alone or with an authentic sample. The colorless product was 2,2′-diethylhydrazobenzene, m.p. 107–108° alone or with an authentic sample.

4,4′-Diethylhydrazobenzene

When 4,4′-diethylhydrazobenzene (0.09 g) was dissolved in ethanol and the solution was boiled for several minutes, an orange color developed. Evaporation produced orange crystals, m.p. 57–58°. Repeated recrystallizations from ethanol gave 4,4′-diethylazobenzene, orange needles, m.p. 60–61° alone or with an authentic sample.

4,4′-Diethylhydrazobenzene (0.05 g) was allowed to stand in air for several days and was oxidized to 4,4′-diethylazobenzene, m.p. 58–60° alone or with an authentic sample.

Spectra

The infrared spectra were recorded on a Perkin–Elmer Infracord model 137B spectrophotometer. The spectra of the diethylazoxybenzenes were obtained from liquid samples and those of the diethylhydrazobenzenes by the potassium bromide pellet technique. The other infrared spectra were recorded by employing Nujol mulls. The visible and ultraviolet spectra were determined on a Beckman model DK-2 ratio-recording spectrophotometer, using absolute ethanol as solvent.

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